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Remarks

Amendments to the Claims

Claim 21 has been amended to recite a method of de-inking waste printed paper, comprising: (a) pulping at a pH between 3 and 8 waste printed paper with an enzyme capable of dislodging ink particles from the waste printed paper in an aqueous medium at a pH between 3 and 8, wherein ink is dislodged from the waste printed paper by action of the enzyme; and (b) removing the dislodged ink particles from the resulting pulp containing medium.

Claim 31 has also been amended to recite a method of recycling waste printed paper comprising: (a) pulping at a pH between 3 and 8 waste printed paper with an enzyme capable of dislodging ink particles from the waste printed paper in an aqueous medium at a pH between 3 and 8, wherein ink is dislodged from the waste printed paper by action of the enzyme; and (b) removing the dislodged ink particles from the resulting pulp containing medium. Claim 31 has also been amended to refer to high wastepaper pulping consistency (referred to in the specification and claims as "high pulp content").

Support for the amendments is found, for example, at page 6, lines 7-8, and original claim 8, of the priority application, U.S.S.N. 07/518,935 filed May 4, 1990 ("the '935 application), claiming priority to Korean application 6514/1989 filed May 16, 1989. The Korean application is identical to the '935 application, with the exception of the paragraph found on page 6, at lines 25-27 of the '935 application, which was added to the Korean application. Support for the range 3 to 8 is found on page 8-2, last paragraph, line 6. Support for the high pulping

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consistency is found on page 8-2, last paragraph, line 3. A copy of the '935 application and the originally filed English translation of the Korean patent application as well as a new translation of the Korean patent application are enclosed. The original Korean patent application was downloaded from the Korean patent application site and a new translation prepared to insure the accuracy of the translation.

Applicants are therefore fully entitled to the priority date of May 16, 1989, for the range of 3 to 8 in claims 21 and 31.

Claim 29 has been cancelled.

The phrase "a temperature of 20°C" in claim 30 was added May 13, 1991 by amendment. Claims 30, 32 and 40 have been amended to refer to "room temperature" (which could encompass of temperature of between about 20-25°C) and is therefore fully entitled to the priority date of May 16, 1989.

Claims 25 and 34 have been amended to recite only cellulases and pectinases, which is fully supported in the May 16, 1989 priority application.

The phrase "pH 3 to about 7" and "pulping at an acid or neutral pH" was not originally disclosed in 07/518,935 but is found at page 6, lines 6-7 of US.S.N. 08/239,313 which was filed on May 6, 1994 (the '313 application"). Therefore claims 26 and 35 are entitled to a priority date of May 6, 1994.

Claims 27 and 37 have been amended to define the aqueous medium where alkali ("caustic soda" as originally translated) is not added. This is fully supported by the priority date

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of May 16, 1989, at page 8-2, paragraph 6, lines 4-5. Claims 41 and 47 have been amended to recite a pH range of between 3 and 8 and are therefore fully entitled to the priority date of May 16, 1989.

Rejection Under 35 U.S.C. § 102

a. Japanese Patent Document No. JP-A 59-9299

Claims 21-25, 27-34, and 36-47 were rejected under 35 U.S.C. § 102(b) as being anticipated by or, in the alternative, under 35 U.S.C. 103(a) as obvious over Japanese Patent Document No. JP-A 59-9299 published 1984 ("the '299 patent"). Applicants respectfully traverse this rejection

The '299 patent describes a de-inking agent that can be used for recycling of old paper such as newspapers and magazines. The de-inking agent contains a cellulase (page 2, 4th paragraph). Cellulases are commonly found in animals, plants, bacteria, and fungi. The '299 patent discloses that alkaline cellulases are especially preferred. The '299 patent defines an alkaline cellulase as one having an optimum activity between pH 8.0 an 11.5. There is a statement that "Such enzymes retain their activity in the alkaline region as well as the acid and neutral range" (bottom of page 2 to top of page 3). The Examiner has alleged that since the enzyme can be active in acidic and neutral pH, it would have been obvious to use the cellulase over its entire range of activity, e.g. at acidic and neutral pH. The examiner's reasoning is in error since the claimed pH range is to the pH of the pulp; the prior art comment relates to the pH at which the enzyme is active. The statement merely implies that one can use an enzyme with a

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broad pH specificity or more preferably one with a pH optimum between 8-11; there is nothing with respect to the pH of the pulp to which the enzyme is added.

In determining the differences between the prior art and the claims, the question under 35 U.S.C. 103 is not whether the differences themselves would have been obvious, but whether the claimed invention as a whole would have been obvious **to one of ordinary skill in the art at the time of the invention.** *Stratoflex, Inc. v. Aeroquip Corp.*, 713 F.2d 1530, 218 USPQ 871 (Fed. Cir. 1983); *Schenck v. Nortron Corp.*, 713 F.2d 782, 218 USPQ 698 (Fed. Cir. 1983). To establish *prima facie* obviousness of a claimed invention, all the claim limitations must be taught or suggested by the prior art. *In re Royka*, 490 F.2d 981, 180 USPQ 580 (CCPA 1974). "All words in a claim must be considered in judging the patentability of that claim against the prior art." *In re Wilson*, 424 F.2d 1382, 1385, 165 USPQ 494, 496 (CCPA 1970).

Examples 1-3 of the '299 patent all disclose the use of NaOH during the disintegration step. This would yield an alkaline pH (i.e., greater than pH 8.0).

The claims are drawn to a process of deinking at a pH between 3 and 8. The '299 patent does not disclose deinking at a pH between 3 and 8. The examiner is confusing the pH range of the enzyme with the pH range of the deinking process. However, it is the pH range of the deinking process that is in issue.

In Howard Kaplan's declaration (copy enclosed as Exhibit A), which was submitted with the response filed on November 22, 2004 and a copy of which is enclosed with this response, it was shown that the pH of the reaction mixture described in Example 2 of the '299 patent was

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10.6 (alkaline). Although the examiner indicates he is confused by what conditions were used, the conditions that were used were exactly those described in Example 2 of the '299 patent. This is what the undersigned asked the examiner if the applicants should use, and the examiner had stated that was correct. It was also noted that it was impossible to do anything else, as requested by the examiner, since what the examiner was requesting was not disclosed in the '299 patent.

The Japanese Patent Office (JPO), in its Decision of Opposition to Patent (copy enclosed as Exhibit B), a registered copy of which was submitted with the response filed on August 11, 2004, found that there was no disclosure or suggestion of "pulping after controlling the pH in the range of 3 to 8, a part of the construction of the present invention....Thus the present invention cannot be constructed to be easily inventable by a person having ordinary skill in the art from the description of the '299 patent."

The declarations of Drs. Eriksson and Eveleigh (copies enclosed as Exhibits C and D), dated March 19, 2004 and April 12, 2004, respectively, state that it is their understanding that the '299 patent discloses only the successful use of deinking enzymes with alkaline deinking chemicals such as sodium hydroxide. Dr. Eriksson cites an article from Paper and PulpInternational (PPI) entitled "Neutral Deinking Makes Its Debut" (copy enclosed as Exhibit E) describing the breakthrough in October 1993 of deinking in neutral conditions, without the addition of alkalis such as sodium hydroxide to the pulp prior or during deinking. The declaration of Mr. Schmid (copy enclosed as Exhibit F), dated May 7, 2004, states that it is his

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understanding that there was no suggestion of non-alkaline deinking at the Zwingen plant prior to 1992.

In summary:

The '299 patent does not disclose deinking at a pH between 3 and 8. The '299 patent discloses deinking using an enzyme that has activity over a range of 3 to 11, preferably 8.1-11.

The Japanese Patent Office Opposition Board found that the '299 patent did not disclose deinking of paper pulp with an enzyme at a pH of 3 to 8.

Those skilled in the art believed that it was believed that one could only deink at an alkaline pH at the time this application was originally filed.

Accordingly, the applicants have clearly shown that there was no suggestion in the prior art of enzymatic deinking at a pH of 3 to 8 – i.e., at an acid or neutral pH. Accordingly, the claims are novel and inventive over the '299 patent.

b. Japanese Kokai 63-59494

Claims 21-25, 27-34 and 36-47 were rejected under 35 U.S.C. 102(b) as anticipated by or, in the alternative, under 35 U.S.C. 103 (a) as obvious over Japanese Kokai 63-59494 ("JP '494").

The Examiner alleges that JP '494 discloses de-inking wastepaper using cellulase having a pH within the claimed range. This is simply not accurate.

JP '494 discloses a method of removing ink from used paper, characterized by the use of an ***alkali-resistant*** cellulase in the process of removing ink by treating used paper with ink

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removal chemicals (the bottom of page 3 bridging the top of page 4). JP '494 states that the ink removal reaction proceeds ***under basic conditions***. JP '494 describes a method in which the alkali resistant cellulase can be added 30 minutes to one hour after the addition of the usual ink-removal chemicals, or can be added simultaneously with the ink-removal chemicals (page 5, 1st paragraph). The ink removal chemicals described are those chemicals generally used to remove ink from used paper. Examples include alkali such as NaOH and Na_2CO_3, silicic acid soda, hydrogen peroxide, phosphate, anionic and non-ionic surface active agents, scavengers such as oleic acid and additional agents such as pH stabilizers, chelating agents, and dispersants (the bottom of page 5 bridging the top of page 6). Example 1 describes a method of treating used newspaper using 1% NaOH, 1% H_2O_2, 3% silicic acid soda and 0.2% of a non-ionic surface-active agent. The mixture was stirred for 20 minutes at 50°C and 0.1% alkaline resistant cellulase was added. The mixture was diluted to a 1% concentration and flotation was carried out for 10 minutes using a testing flotation device. After the reaction was completed, 100 g/m^2 of handmade paper was obtained by ***maintaining the pH as is (pH 9.1)*** (top of page 7). Example 2 describes a method of treating similar or transliteration paper using 1% NaOH, 0.1% nonionic surface-active agent and 0.05% alkali-resistant cellulase (same enzyme used in Example 1). Example 3 describes a method of treating used newspaper using 1% NaOH, 0.1% non-ionic surface-active agent, and 0.5% alkaline-resistant cellulase. In Example 1, the cellulase was added after the addition of the ink-removing chemicals. In Examples 2 and 3, the cellulase was

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added simultaneously with the ink removing chemicals. JP '494 clearly does not disclose a method of enzymatically deinking waste printed at a pH between 3 and 8.

The Examiner is directed to the declaration of Dr. Masahiro Samejima (copy enclosed as Exhibit G), dated March 5, 1996, which was submitted during prosecution of related application U.S.S.N. 08/239,313 ("the '313 application") as well as the letter from Mr. Kouichiro Takaku (copy enclosed as Exhibit H), a Japanese Patent Attorney, dated January 24, 1996, which was also submitted during prosecution of the '313 application. Dr. Samejima and Mr. Takaku both stated that the JP '494 patent states that "Cellulase is inactivated in an alkali condition of pH 8 or more. On the other hand, as a deinking is performed in the alkali condition, conventional cellulase cannot use therefore."

This can only be interpreted to state that the deinking described by the JP '494 is performed at a pH of greater than 8, i.e., under alkaline conditions.

The declarations also state that the JP '494 says "On the other hand as a deinking is performed in the alkali condition, conventional cellulase cannot use therefore. However, in case alkali-resistant cellulase is used, it is activatable in the alkali condition. Therefore, if the deinking is performed by using alkali-resistant cellulase with a deinking agent (alkali), the deinking effect is improved due to the action of the enzyme." This clearly indicates that one must use a cellulase that is active at alkaline conditions.

However, the claim *of the present application* is drawn to

A method of de-inking waste printed paper, comprising

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a) **pulping at a pH between 3 and 8 waste printed paper** with **an enzyme capable of dislodging ink particles from the waste printed paper in an aqueous medium at a pH between 3 and 8**, wherein ink is dislodged from the waste printed paper by action of the enzyme; and

b) removing the dislodged ink particles from the resulting pulp containing medium.

Note the requirement both of the pH of the pulping conditions and of the requirement that an enzyme be used which is active at a pH of 3 to 8. This is simply not disclosed by nor obvious from the JP '494.

c. WO 91/14819

Claims 21-25, 27-34 and 36-47 are rejected under 35 U.S.C. 102(b) as anticipated by or, in the alternative, under 35 U.S.C. 103 (a) as obvious over WO 91/14819 to Baret *et al.* ("the '819 application").

As amended, all claims with the exception of claims 26 and 35 are fully entitled to a priority date of 1989. WO 91/14819 is therefore not prior art to claims 21-25, 27-34 and 36-47. Claims 26 and 35 have not been rejected over WO 91/14819.

Rejection Under 35 U.S.C. § 103

a. Japanese Patent Document No. JP-A 59-9299 with or without U.S. Patent No. 3,966,543 or U.S. Patent No. 4,618,400.

Claims 21-47 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Japanese Patent Document '299 alone or in combination with U.S. Patent No. 3,966,543 to Cayle

et al. ("Cayle") or U.S. Patent No. 4,618,400 to Wood *et al.* ("Wood"). Applicants respectfully traverse these rejections.

As discussed above, the '299 patent does not disclose or suggest deinking at a pH between 3 and 8 using a cellulase that is active at a pH between 3 and 8. As defined by Webster's third New International Dictionary (pages enclosed), "between" is defined as "in intermediate relation to in respect to quantity, quality or degree". Accordingly, "a pH between 3 and 8" means a pH of greater than 3 and up to 8.

Cayle describes a method for the treatment of paper *to facilitate its disintegration upon subsequent disposal* (col. 1, lines 4-6). The method comprises applying a dilute aqueous solution of a cellulase enzyme complex to the wet paper web during paper manufacture (col. 1, lines 23-30). The cellulase complex can be obtained from various natural sources and particularly microbial sources including *Trichloderma viride, Penicilium variable,* and *Myrothecium verrucaria* (col. 3, lines 12-17). Cayle does not disclose or even suggest a method for *de-inking* wastepaper wherein the ink is detached from the fibers so that they can be efficiently removed in much less a method for de-inking waste paper at acidic or neutral pH. Deinking is the detachment of ink from the paper fibers so that they can be efficiently removed from the waste water. Merely defibering waster paper with ink still attached to the fibers, as described by Cayle, does nothing to facilitate deinking. Cayle does not provide the elements missing from the '299 patent.

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Wood describes a method for the de-inking of wastepaper which comprises converting the wastepaper to a pulp, contacting the pulp with an aqueous medium of *alkaline pH* containing between about 0.2 and 2 percent by weight, calculated on dry weight of the pulp, of a de-inking agent which is one or a mixture of certain thiol ethoxylate compounds, and treating the resulting pulp-containing medium to remove the suspended or dispersed ink (col. 1, line 57 to col. 2, line 12). Wood does not disclose an enzymatic method for de-inking wastepaper at acidic or neutral pH.

Therefore neither Wood nor Cayle make up for the deficiencies of the '299 patent.

b. GB 2,231,595 or WO 91/14819 in view of Japanese Kokai 63-59494

Claims 26 and 35 were rejected under 35 U.S.C. 103(a) as obvious over GB 2,231,595 ("the '595 application") or WO 91/14819 ("the '819 application') in view of Japanese Kokai 63-59494 ("the JP '494 patent").

The '595 application is the equivalent of the parent application, 07/518,935 ("the '935 application"). The '595 application discloses a method for de-inking waste printed paper, comprising: a) pulping at a pH in the range of 3 to 8 waste printed paper with an enzyme capable of dislodging ink particles from the waste printed paper in an aqueous medium at a pH in the range of 3 to 8, wherein ink is dislodged from the waste printed paper by action of the enzyme. The '595 application does not disclose cellulases derived from *Trichoderma viride*, *Aspergillus niger* and mixtures thereof.

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The '819 application discloses an enzymatic process for deinking waste paper, comprising the following sequential steps: (a) pulping the wastepaper at a consistency above 8% in the presence of deinking chemicals *at a pH above 9.5*; (b) lowering the pH to 6-9.5 by addition of an acidifying agent and adding **alkaline cellulase**; (c) continuing the pulping and/or maceration at consistency above 8%; and (d) separating the ink particles from the pulp.

As discussed above, JP '494 discloses the use of an alkaline-resistant cellulase *under alkaline conditions (i.e. addition of sodium hydroxide)* to de-ink wastepaper. The JP '494 patent does not disclose or suggest a method of de-inking waste printed paper, comprising: a) pulping at a pH *in the range of 3 to 8* waste printed paper with an enzyme capable of dislodging ink particles from the waste printed paper in an aqueous medium *at a pH in the range of 3 to 8*, wherein ink is dislodged from the waste printed paper by action of the enzyme (see the declaration of Dr. Masahiro Samejima, dated March 5, 1996 and the letter from Mr. Kouichiro Takaku, dated January 24, 1996, copies of which are enclosed).

None of the cited art discloses the claimed cellulases derived from *Trichoderma viride*, *Aspergillus niger*. None of the prior art provides any motivation to obtain the claimed cellulases and combine them with the claimed process as applicants have done. None of the art cited by the examiner would lead one of skill in the art to modify what is disclosed to use the claimed enzymes, with a reasonable expectation of success. Therefore claims 26 and 35 are not obvious over the cited art.

Allowance of claims 21-28, 30-38, and 40-47 is respectfully solicited.

Respectfully submitted,

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Background of the Invention

1. Field of the Invention

This invention relates to a process for reclaiming useful pulp fibers from wood-containing or wood-free wastepaper by a biological method in the de-inking process.

2. Description of the Background

De-inking of pulp fibers is essentially a laundering or cleaning process in which the ink is considered to be the dirt.

Chemicals, along with heat and mechanical energy, are used to dislodge the ink particles from fibers and to disperse them in the aqueous medium. The ink particles are then separated from the pulp fibers, either by washing or flotation or by using a modern hybrid process that combines washing and flotation.

The chemicals used for the conventional de-inking process are surfactants which function as detergents to remove ink from the fiber, as dispersants to keep the ink particles dispersed and prevent redeposition on the fibers, and foaming agents in the froth flotation of ink particles.

A typical surfactant is a long chain molecule with a hydrophobic part on one end and a hydrophilic part on the other end. The hydrophobic part may consist of fatty acid, fatty alcohol, alkylphenols or other oil-soluble surfactants.

The hydrophilic part in the de-inking surfactant usually consists of anionic molecules, such as carboxylic acid salts or sulfonic acid salts and nonionic molecules, such as polyoxyethylenated chains.

The typical surfactants commonly used in the washing and froth flotation de-inking processes are: sodium and potassium salts of straight-chain fatty acids (soaps), linear alkylbenzenesulfonates (LAS), long-chain fatty alcohols, polyoxyethoxylated alkylphenols, alkylphenol-ethoxylates, and polyoxyethoxylated straight-chain alcohols.

A major disadvantage of using these surfactants in the de-inking process is excess foaming in the subsequent pulp stock flow and papermaking process lines. Moreover, some of

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the above surfactants are resistant to biodegradation in the effluent treatment stages causing a serious environmental problem.

In the froth flotation de-inking process, a collector is added to agglomerate ink into large particles and attach them to the air bubbles. Collectors are required for effective flotation and are usually anionic long-chain fatty acid soaps. Fatty acid collectors are precipitated with calcium ions to form larger, insoluble ink particles and collector particles. With injection of air in the flotation cells, the agglomerated ink particles adhere to the bubbles, rise to the surface and are skimmed off from the system.

Major disadvantages of the flotation method using the fatty acid collector are a pitch deposition and calcium scaling problems in the subsequent stock lines and papermaking process equipment. Besides surfactants, other chemicals employed are caustic soda, sodium silicate, metal ion chelating agents and hydrogen peroxide.

The hydrogen peroxide bleaching agent has to be added in order to prevent pulp yellowing caused by the addition of caustic soda and to improve the brightness of pulp fibers.

With advances in modern printing and photocopying technology, conventional de-inking with the aid of surfactants encounters serious problems because the wastepaper is printed with the use of heavily coated, highly polymerized or non-impact inks, such as ultraviolet, heat-set, Xerox, laser and ink jet. These inks usually contain cured polymer resins which bind ink particles so strongly on the fiber surface that it is impossible to dislodge the inks completely during the wastepaper defiberizing (pulping) stage with the conventional de-inking chemicals. Excess heat and mechanical energy are also required along with the ineffective conventional chemicals.

Furthermore, in the conventional flotation de-inking process for newsprint wastepaper, a major technical problem has to do with the fact that fine ink particles are embedded in the fiber bundles and between fibrils which are almost impossible to be removed from the fibers by a washing and/or

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flotation process.

Summary of the Invention

This invention provides a new and much improved de-inking method which is effective for newsprint as well as wood-free printed wastepaper, such as whiteledger, laser printed, xerographic copypaper and computer printout wastepaper.

The de-inking method of the present invention is to remove ink particles by the use of the biological activity of enzymes on the cellulose fiber surface and the dispersing function of enzyme protein on ink particles.

In contrast to the conventional method, no alkali or de-inking surfactants are required, although some surfactants can be used along with the enzyme to enhance the de-inking efficiency. In the froth flotation process, the fatty acid collectors are not required. Since caustic soda is not used in the newsprint de-inking, a hydrogen peroxide bleaching agent is also not required for preventing yellowing.

The elimination of the fatty acid collector in this biological de-inking process will solve the persistent pitch and scale deposition problem associated with the conventional flotation process using the fatty acid type soap and calcium salts and silicates.

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Description of the Preferred Embodiment

The wastepaper, such as old newsprint, is disintegrated in a conventional pulper (consistency 4-7%) or in a high consistency pulper, (consistency 12-15%), at a water temperature ranging from room temperature (20°C-25°C) up to 60°C. The addition level of enzyme is 0.005% to 5.0% by weight based on dry weight of wastepaper. The pH of the stock slurry is adjusted in the range of 3.0 to 8.0. As compared to the conventional pulping process using caustic and surfactants, the pulping in the presence of enzyme can be completed in a relatively short period and ink particles are completely separated from the fiber surface and dispersed well. The dispersed inks are removed out of the pulp fibers by using the conventional washing process equipment, such as vibrating screen and drum washers without the aid of detergent surfactants in single and multi-stages. The ink particles dispersed with the action of enzyme protein can be also selectively removed out of the diluted pulp slurry with conventional flotation equipment in which air is injected or drawn into the pulp to provide bubbles to pick up the particles. No fatty acid collector is required in the case of waste newsprint. A small amount of fatty acid collector may be added to enhance the ink removal efficiency in the case of laser-printed wastepaper.

Among enzymes which can be used in the method are the carbohydrases and particular enzymes, such as cellulase, hemicellulase, pectinase and mixtures thereof.

This biological de-inking process lowers pulping energy requirements to a large extent (almost 50% reduction) since the addition of enzyme results in a substantial reduction in pulping time as compared to the pulping in the absence of enzyme. The observed faster and easier pulping in the presence of enzyme may be attributed to the unique biological activity of the enzyme which is effective to debond the fiber bonding and dislodge the inks bonded on the fiber surface as well as within the fiber bundles or between the fibrils. A partial enzymatic hydrolysis of cellulose within the micro structure of the fiber surface may occur

during the pulping stage. Because of this biological activity of the enzyme, the fine ink particles embedded within fiber bundles, fibrils and fines which have been impossible to be taken out by the conventional de-inking chemicals in the case of old newsprint de-inking are removed.

According to this biological de-inking method of old newsprint, the addition of hydrogen peroxide to prevent fiber yellowing is not required. This results in a substantial reduction of de-inking chemical cost as compared to the conventional de-inking process using caustic soda, hydrogen peroxide, chelating agents and sodium silicates.

It should be pointed out that the physical strength properties of the resulting pulp fiber prepared by this invented method are found to be higher than those of the corresponding pulp prepared by the conventional method in addition to the much higher resulting pulp brightness. The enzyme addition does not appear to degrade the fiber strength, but rather improves the fiber strength for reasons not presently known.

To more fully illustrate the present invention, the following non-limiting examples are presented.

<u>Example 1</u>

<u>De-inking of Old Newsprint with a Cellulolytic Enzyme</u>.

A sample of old newsprint wastepaper was added to the pulper which was filled with 40°C water at a consistency of 4% and (a) cellulase (enzyme) was dissolved at the dosage level of 0.1% based on oven dry weight of wastepaper. The wastepaper was soaked for 10 minutes and then disintegrated for 5 minutes. After a complete disintegration of wastepaper, one half of the pulp slurry was diluted to 1% consistency.

The diluted pulp slurry was moved to the air flotation cell and then the dispersed ink particles were removed out of the pulp slurry by skimming off the ink particles froth out of the cell while injecting air through a porous plate. The flotation time for the complete removal of the

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ink froth was one minute.

The other half of the pulp slurry was washed on a laboratory vibrating screen to remove the dispersed ink particles.

The resulting recycled pulp fibers obtained by the flotation and the washing step were evaluated for pulp brightness and mechanical strength properties. To compare this enzyme-treated de-inked pulp to the conventional de-inked pulp, the same sample of wastepaper was treated in the pulper with addition of 1.0% NaOH, 0.3% H_2O_2, 3% sodium silicate solution (water glass) and 0.8% of SERFAX MT-90 (fatty acid soap) and 0.2% IGEPAL-660 (biodegradable nonionic surfactant marketed by GAF Corporation) based on oven dry weight of wastepaper. The pulping time was 10 minutes for a complete disintegration. After diluting to 1% consistency, the dispersed ink particles were removed by the flotation method with the laboratory flotation cell as described above.

As shown in Table 1, the brightness of the pulp de-inked with enzyme was much higher than that of the pulp de-inked with the conventional chemicals and the mechanical strength of the enzyme-de-inked pulp was also superior to the pulp de-inked with the fatty acid collector and the dispersant (IGEPAL-660). Microscopic observation revealed that the pulp prepared by the present invention contained more long fiber fractions, has smoother fiber surface and looks less mechanically damaged.

Table 1. Comparison of properties of recycled pulp by the method of the present invention and the conventional method.

		brightness (%)		tensile index (N.m/g)		tear index (mN.m/g)	
		KONP	AONP	KONP	AONP	KONP	AONP
present method	flotation	47.1	45.2	28.9	32.4	11.7	13.6
	washing	50.3	48.6	29.3	32.9	11.8	14.1
conventional method		45.1	38.4	30.1	32.8	10.8	13.1

KONP: Korean old newspaper
AONP: American old newspaper

As can be seen from the data in Table 1, the enzyme-treated pulp gave cleaner and brighter pulp with the washing as compared to the flotation ink removal using the conventional method.

The enzyme addition also appeared to accelerate the wastepaper disintegration to a large extent. When the old newspaper was disintegrated in the conventional pulper at the 4% consistency, the addition of 0.5% enzyme reduced the pulping time from 5 minutes (no enzyme addition) to 30 seconds for a complete disintegration as shown in Table 2.

Table 2. Relation between enzyme addition and disintegration time.

enzyme (%) (cellulase)	0.5	0.1	0
disintegration time (sec)	30>	60-120	300<

Example 2

De-inking of Laser CPO (computer printout) with Cellulolytic enzyme.

It is almost impossible to achieve a complete removal of laser beam cured ink particles from the laser CPO wastepaper with the conventional de-inking chemicals, because the ink particles are so strongly adhered to the fiber surface that alkali and general de-inking surfactants used in the conventional process are not able to dislodge and disperse the ink in the pulp-water slurry.

A sample of laser-CPO wastepaper was added to water in a laboratory high consistency pulper to achieve a consistency of 12.5% and a cellulase (enzyme) was added to the water at the dosage level of 0.2% based on the dry weight of paper. At stock water temperature of 20-35°C, the pulping was carried out for 20 minutes. The completely disintegrated pulp slurry was diluted to 0.5% consistency and then the dispersed ink particles were removed out of the pulp slurry using the laboratory flotation cell in the same way described in Example 1. In this case, to increase the ink removal efficiency and selectivity, a small amount of the conventional fatty acid collector, SERFAX MT-90, 0.3% based on dry weight of wastepaper, was added prior to the air flotation step and the flotation time was 3 minutes. To compare to the enzyme de-inked pulp, the conventional de-inked pulp was prepared by the same way but the following chemicals and conditions were used:

1% NaOH on dry weight of wastepaper
0.1% IGEPAL-660 dispersant
0.8% SERFAX MT-90
pulping temperature: 50°C
pulping time: 30 minutes
calcium salt addition to the flotation cell: 200ppm
flotation time: 3 minutes

The brightness and the strength properties of the resulting pulp samples were compared in Table 3.

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Table 3. Comparison of pulp properties recycled by the method of the present invention and the conventional method.

	brightness (%)	dirt amount (count/area)	tensile index (N.m/g)
enzyme + MT-90(0.3%)	79.0	450	34.3
MT-90 (0.8%) (conventional method)	80.6	4,330	26.3

Example 3

De-inking of waste newsprint by pectinolytic enzyme.

As per the method of Example 1, the waste newsprint containing 0.1% of pectinase was soaked for 10 minutes at 40°C and disintegrated for 5 minutes. The disintegrated pulp was diluted to a consistency of 1%. Ink particles were removed by flotation for 1 minute.

As shown in Table 4, the brightness and the tensile strength of paper sheet prepared by the method of the present invention are improved.

Table 4. Comparison of the method of using pectinolytic enzyme with the conventional method.

	brightness (%)	tensile index (N.m/g)
present method	44.2	33.3
MT-90 (0.8%) (conventional method)	38.4	32.8

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The foregoing disclosure and description of the invention is illustrative and explanatory thereof, and various changes in the method steps may be made within the scope of the appended claims without departing from the spirit of the invention.

What Is Claimed Is:

Sub B1

1. A method of de-inking wastepaper comprising pulping waste printed paper with an enzyme capable of dislodging ink particles from the pulped paper and removing dislodged ink particles.

2. The method of Claim 1 wherein said ink particles are removed by flotation.

3. The method of Claim 1 wherein said ink particles are removed by washing.

4. The method of Claim 1 wherein said enzyme is selected from the class consisting of cellulase, hemicellulase, pectinase ~~and~~, other carbohydrases ~~or~~ and mixtures thereof.

5. The method of Claim 1 wherein the amount of enzyme used is in the range of 0.005% to 5% by weight based on the dry weight of the wastepaper.

6. The method of Claim 2 wherein the amount of enzyme used is in the range of 0.005% to 5% by weight based on the dry weight of the wastepaper.

7. The method of Claim 1 including controlling the temperature of the pulping process in a range of from room temperature up to about 60°C.

8. The method of Claim 1 including controlling the pH of the pulping process in a range of from 3 to 8.

add a2

Abstract of the Disclosure

A method of de-inking wastepaper by pulping the paper in the presence of an enzyme which dislodges the ink particles from the paper fibers and removing the dislodged ink particles by a method, such as flotation or washing.

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This is to certify that the annexed is a true copy from the original records of the following application as filed with this office.

Application Number : 6514/1989

Date of Application : May. 16, 1989

Applicant(s) : Korea Research Institute of Chemical Technology

Sep. 14, 1990

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The Title of Invention

Biological Deinking Method

1. The title of the invention

Biological deinking method.

2. Detail description of the invention

This invention related to the process for reclaiming useful pulp fibers from wood containing or wood free wastepaper by a biological method in the deinking process.

Deinking of pulp fibers is essentially a laundering or cleaning process which the ink is considered to be the dirt. Chemicals along with heat and mechanical energy, are used to dislodge the ink particles from fibers and to disperse them in the aqueous medium. The ink particles are then separted from the pulp fibers, either by washing or flotation or by using a modern hybrid process that combines the two elements.

The chemicals used for the conventional deinking process are surfactants of which functions are detergency to remove ink from fiber, dispersing action to keep the ink particles dispersed prevent redeposition on the fibers, and foaming action in the froth flotation of ink particles. A typical surfactant is a long chain molecules with the hydrophobic part to the one end and the hydrophilic part to the other end. The hydrophobic part may be consisted of fatty acid, fatty alcohol, alkylphenols or other oil-soluble surfactants. The hydrophilic part in the deinking surfactant usually consists of aninon molecules such as carboxyl acid salts or sulfonic acid salts and nonionic molecules such as polyoxyethylenated chains. p.1 New

The typical surfactants commonly used in the washing and froth flotation deinking processes are ; sodium and potassum salts of strait-chain fatty acid (soap), linear alkylbenzenesulfonate(LAS), - olefine sulfonate, long-chain fatty alcohol, polyoxyethylenenated alkylphenols, alkylphenolethoxylates, and polyoxyethylenated strait-chain alcohols. Major disadvantages of using these surfactants in the deinking process are excess foaming in the subsequent pulp stock flow and papermaking process lines. Some of the above surfactants are resistant to biodegradation in the effluent treatment stages causing a serious environmentel problem. In the froth flotation deinking process, a collector is added to agglomerate ink into large particles and attach them to the air bubbles. Collectors are required for effective flotation and are usually anionic long-chain fatty acid soap. Fatty acid collectors are precipitated with calcium ions to form larger, insoluble ink particles and collector particles. With injection of air in the flotation cells, the agglomerated ink particles adhere to the bubbles, rise to the surface and are skimmed off from the system. Major disadvantages of the flotation method using the fatty acid collector is a pitch deposition and calcium scaling problems in the subsequent stock lines and papermaking process equipments.

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Besides the surfactants, other chemicals are caustic soda, sodium silicate, metal ion chelating agents and hydrogen peroxide.
The hydrogen peroxide bleaching agent has to be added in order to prevent a pulp color yellowing caused by the addition of caustic soda and to improve brightness of pulp fibers.

When an advance in the mordern printing and photocopying technology the conventional deinking with the aid of surfactants encounters serious problems with the wastepaper printed with the use of heavily coated, highly polymerized, or nonimpact inks, such as ultraviolet, heatset, Xerox, laser and ink jet. These inks usually contain cured polymer resins which bind ink particles so strongly on the fiber surface that it is impossible to dislodging the inks completely during the wastepaper defiberizing (pulping) stage with the conventional deinking chemicals. Excess heat and mechanical energy are also required along with the ineffective conventional chemicals.

In the conventional flotation deinking process for newsprint wastepaper a major technial problem has something to do with the fine ink particles embeded in the fiber bundles and between fibrils which are almost impossible to be removed from the fibers by a washing and/or flotation process.

This invention provides a new and much improved deinking method which is effective in the newsprint deinking as well as the wood free printed wastepaper such as whiteledger, laser printed, xerographic copypaper and computer printout wastepaper.
This invented deinking method is to remove ink paticles with the use of biological activity of enzyme on the cellulose fiber surface and a dispersing function of enzyme protein on ink paticles. — end p. 2 Newtrand

In contrast to the conventional method no alkali and deinking surfactants are required although some surfactants can be used along with the enzyme to enhance the deinking efficiency. In the froth flotation process the fatty acid collectors are not required. Since caustic soda is not used in the newsprint deinking, hydrogen peroxide bleaching agent is not also required for the yellowing prevention.
The elimination of the fatty acid collector in this biological deinking process will solve the persistent pitch and scale deposition problem associated with the conventional flotation process using the fatty acid type soap and calcium salts and silicates.
The invented process is described in details as follows:
The newspaper such as old newsprint or printed wood free wastepaper is disintergrated in the conventional pulper (consistancy 4-7%) or in the high consistency pulper, 12-15%, at the water temperature ranged from room temperature up to 60 C. The addition level of enzyme is 0.005% to 5.0% based on dry weight of wasepaper, pH of the stock slurry is adjused in the range of 3.0 to 8.0. As compared to the conventional pulping process using caustic and surfactants the pulping in the process of enzyme can be completed in a relatively short period and ink particles are completely seperated from the fiber surface and dispersed well.. The dispersed inks are removed out of pulp fibers by the conventional washing process equipments such as vibration screen and drum washer without an aid of detergent surfactants in a single and multi stages. The ink patricles dispersed with the action of enzyme protein can be also selectively removed out of the diluted pulp slurry with conventional flotation equipments which air is injected or drown into pulp to provide bubbles to pick up the particles. No fatty acid

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collector is required in the case of waste newsprint. But the small amount of fatty acid collector may be added to enhance the ink removal efficiency in the case of laser-printed wastepaper.

end of p. 3 new transl.

This biological deinking process is to lower pulping energy to a large extent since the addition of enzyme resulted in a substantial reduction in pulping time as compared to the pulping in the absence enzyme, almost 50% reduction. The observed faster and easier pulping in the presence of enzyme may be attributed to an unique biological activity of enzyme which is effective to debond the fiber bonding and dislodge the inks bonded on the fiber surface as well as within the fiber bundles or between the fibrils. A partial enzymatic hydrolysis of cellulose within micro structure of fiber surface may occur during the pulping stage. Because of this biological activity of enzyme the fine ink particles embeded within fiber bundles, fibrils and fines which has been impossible to be taken out by the conventional deinking chemicals in the case of old newsprint deinking.

According to this biological deinking method of old newsprint, the addition of hydrogen peroxide to prevent the fiber yellowing is not required, which will result in a substantialreduction of deinking chemical cost as compared to the conventional deinking process using caustic soda, hydrogen peroxide, chelating agent and sodium silicates.

It should be pointed out that the physical strength properties of the resulting pulp fiber prepared by this invented method are found to be higher than those of the corresponding pulp prepared by the conventional method in addition to the much higher resulting pulp brightness. The enzyme addition dose not appear to degrade the fiber strength, instead improve the fiber strength by not-yet unknown reasons.

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Example 1.

Deinking of old newsprint with a cellulolytic enzyme.

A sample of old newsprint wastepaper was added to the pulper where was filled with 40 C water at the consistancy of 4% and a cellulase was disloved at the dosage level of 0.1% based on oven dry weight of wastepaper. The wastepaper was soaked for 10 minutes and then disintergrated for 5 minutes. After the complete disintergration of wastepaper, the one half of pulp slurry was diluted to 1% consistency.

The diluted pulp slurry was moved to the air flotation cell and then the dispersed ink particles were removed out of the pulp slurry with skimming off the ink particles froth out of the cell while injecting air through a porous plate. The flotation time for the complete removal of the ink froth was one minute.

The other half of the pulp slurry was washed on a laboratory vibration screen to remove the dispersed ink particles.

The resulting recycled pulp fibers obtained by the flotation and the washing step were evaluated for the pulp brightness and the mechanical strength properties. To compare this enzyme-treated deinked pulp to the conventional deinked pulp, the same sample of wastepaper was treated in the pulper with addition of 1.0% NaOH, 0.3% H O , 3% sodium silicate solution (water glass) and 0.8% of SERFAX MT-90 (fatty acid soap) and 0.2% IGEPAL-660 based on oven dry weight of wastepaper. The pulping time was 10 minutes for a complte disintergration. After diluting to 1% consistency, the dispersed ink particles were removed by the flotation method with the laboratory flotation cell as the way described above.

As shown in Table 1, the brightness of the pulp deinked with enzyme was much higher than that of the pulp deinked with the conventional chemicals and the mechanical strength of the enzyme-deinked pulp was also superior to that pulp deinked with the fatty acid collector and the dispersant (IGEPAL-660). The microscopic observation revealed that the pulp prepared by the present invention contained more long fiber fractions and has smoother fiber surface and looks less mechanically damaged. — end. p. 4 Newtransla

Table 1. Comparison of properties of recycled pulp by method of present invention and the conventional method.

		brightness (%)		tensile index (N.m/g)		tear index (mN.m /g)	
		KONP	AONP	KONP	AONP	KONP	AONP
present method	flotation	47.1	45.2	28.9	32.4	11.7	13.8
	washing	50.3	48.6	29.3	32.9	11.8	14.1
SERFEX MT-90		45.1	38.4	30.1	32.8	10.8	13.1

KONP; Korean old newspaper.
AONP; American old newspaper.

The enzyme treated pulp gave cleaner and brighter pulp with the washing as compared to the flotation ink removal.

The enzyme addition appeared to accelerate the wastepaper disintergration to a large extent. When the old newspaper was disintergrated in the conventional pulper at the 4% consistency, the addition of 0.5% enzyme reduced the pulping time from 5 minutes (no enzyme addition) to 30 seconds for a complete disintergration as shown in Table 2.

Table 2. Relation between enzyme addition and disintergration time.

enzyme (%)	0.5	0.1	0
disintergration time (sec)	30>	60~120	300<

Example 2.

Deinking of laser CPO (computer printout) with cellulolytic enzyme.

It is almost impossible to achieve a complete removal of laser beam cured ink particles from the laser CPO wastepaper with the conventional deinking chemicals, because the ink particles are so strongly adhered to the fiber surface that alkali and general deinking surfactants in the conventional deinking chemicals are not able to dislodge and disperse in the pulp-water slurry.

A sample of laser-CPO wastepaper was added to the water in a laboratory high consistency pulper at the consistency of 12.5% and a cellulase was added to the water at the dosage level of 0.2% based on the dry weight of paper. At stock water temperature up 20-35 C, the pulping was carried out for 20 minutes. The completly disintergrated pulp slurry was diluted to 0.5% and then the dispersed ink particles was removed out of the pulp slurry using the laboratory flotation cell as the same way explaine in Example 1. In this case, to increase the ink removal efficiency and selectivity a small amount of the conventional fatty acid collector, SERFAX MT-90, 0.3% based on dry weight of wastepaper was added prior to the air flotation and the flotation time was 3 minutes. To compare to the enzyme deinked pulp, the conventional deinked pulp was prepared by the same way but the different chemical conditions as follow: — End p.5 New translation

1% NaOH on dry weight of wastepaper
0.1% IGEPAL 660 dispersant
0.8% SERFAX MT-90
pulping temperature ; 50 C
pulping time ; 30 minutes
calcium salt addition to the flotation cell ; 200 ppm
flotation time ; 3 minutes

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The brightness and the strength properties of the resulting pulp samples were compared in Table 3.

As shown in the table, the image analysis of the paper samples indicates that the number of the residual ink particles was much less, about 10 times, for the pulp deinked with the enzyme and the tensile strength was also higher as compared to the pulp prepared with the conventional chemicals.

The recycled chemical pulp of high quality in terms of dirt count and fiber strength properties can be obtained with the use of enzyme in a combination of a small amount of fatty acid collector by the flotation method.

Table 3. Comparison of pulp properties recycled by the method of present invention and conventional method.

	brightness (%)	dirt amount (count/area)	tensile index (N.m/g)
enzyme+NT-90(0.3%)	79.0	450	34.3
NT-90 (90%)	80.6	4,330	26.3

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Example 3.

Deinking of waste newsprint by pectinolytic enzyme.

As the same method to example 1, the waste newsprint containing 0.1% of pectinase was sonked for 10 minutes at 40 C and disintergrated for 5 minute. Diluting the disintergrated pulp to 1%, ink particles are removed by flotation for 1 minute.

As shown in Table 4, the brightness and the tensile strength of paper sheet prepared by method of present invention are improved.

Table 4. Comparison the method of using pectinolytic enzyme with conventional method.

	brightness (%)	tensile index (N.m/g)
present method	44.2	33.3
NT-90 (0.8%)	38.4	32.8

= end p.6 new[illegible]

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What we claimed is ;

1. Biological deinking method characterizing pulping of waste printed paper with enzyme and removing ink particles from fibers by flotation and/or washing method,

2. Biological deinking method characterizing using one kind of enzymes which are cellulase and/or pectinase, in claim 1.

3. Biological deinking method characterizing adding the amount of enzyme in the range of 0.005% to 5% based on dry weight of wastepapers in claim 1 or 2.

4. Biological deinking method characterizing controlling the temperature of pulping process ranged from room temperature upto 60 C in claim 1.

5. Biological deinking method characterizing controlling the pH of pulping process ranged from 3 to 8 in claim 1.

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r s of the following application as filed with this office.

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A on Number

년 월 일: 1989년 5월 16일
D Application

출 원 인: 재단법인 한국화학연구소
Ap (s)

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	성 명		주민등록 번호		국 적
	주 소				
발명의 명칭		고지의 생물학적 탈묵에 의한 재생방법			

외국출원	국명	출원의 종류	출원일자	출원번호	증명서류		우선권주장	
					첨부	미첨부	있음	없음

제8조의 규정에 의하여 위와 같이 출원합니다.

1989 년 5 월 16 일

대리인 변리사 이 돈 상

특허청장 귀하

구비서류 : 1. 출원서 정본 1통, 부본 2통
2. 출원심사청구서 1통
3. 명세서 정본 1통, 부본 2통
4. 위임장 1통

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명 세 서

1. 발명의 명칭

고지의 생물학적 탈묵에 의한 재생방법.

2. 발명의 상세한 설명

본 발명은 고지의 생물학적 탈묵에 의한 재생방법에 관한 것이다.

종래의 고지탈묵방법은 해리된 고지를 계면활성제 및 지방산 비누를 주성분으로 하는 탈묵제를 사용하여 세척법 또는 부상부유법에 의해 섬유로부터 분리된 잉크입자들을 제거시켜 왔다.

그러나 고지원료에 사용된 잉크의 구성성분 및 인쇄기술의 다양화 그리고 고지를 구성하고 있는 펄프의 종류가 다양해짐에 따라 탈묵제의 종류가 복잡해지고 있으며 탈묵방법에도 고도의 기술이 요구되고 있어 탈묵제의 종류와 공정이 복잡해지고 있다.

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Newbrough

Patent/Utility model Detailed Information

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Priority info (Country/Number/Date)	
Title of invention	Biochemical de-inking method in waste paper recycling (BIOLOGICAL DE-INKING METHOD)
Abstract	<Purpose> This invention provides an effective new, improved de-inking method for the de-inking from waste newsprint and other printed paper containing no lignin, namely, white ledger paper, laser printed paper by electrostatic photographic process, and computer printout paper.

<Composition>
Newsprint, such as waste newsprint or waste printed paper containing no lignin, containing common pulp content (4 – 7% concentration) or high pulp content (12 – 15% concentration), is disintegrated in water at temperatures ranging from room temperature to 60°C. The amount of the addition of enzyme is based on the dry weight of waste paper and the enzyme concentration is 0.005 – 5.0%. The pH of the starting slurry is controlled at 3.0 – 8.0. The dispersed ink can be removed from pulp fibers using conventional rinsing apparatus without the aid of a surfactant, namely, by using a vibrating sieve and a drum rinsing apparatus. By the action of enzyme protein, the dispersed ink particles in the diluted slurry can be selectively removed by using a conventional flotation separation apparatus by the action of bubbles, which float up the particles, resulted from the injection of air and the adsorption of the air into the slurry. In the case of waste newsprint, the use of a fatty acid collecting agent is not needed, but in the case of laser printed paper, a small amount of fatty acid collecting agent may be added to improve the de-inking efficiency.
<Effect>
The addition of an enzyme significantly shortens the pulping period and, therefore, the energy consumption for the pulping process can be reduced by almost 50%.

Representative Claim	Waste paper was pulped in the presence of other components, and the ink particles were removed by flotation method or rinsing method. The pulp was made into paper in the recycling of the waste paper after the biochemical de-inking method of waste paper.
Representative Drawing	
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Facsimile Full-Doc.	View Facsimile Full-DOC.
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(54) Biochemical de-inking method in waste paper recycling

Abstract
No abstract

Disclosure
[Title of invention] Biochemical de-inking method in waste paper recycling

[Detailed description of invention] (Industrial applications) This invention pertains to the de-inking process in a biochemical recovery method of valuable pulp fibers from waste paper containing lignin or containing no lignin.

The de-inked ink from the pulp fibers is basically considered as waste, and this process is a waste removal or rinsing process.

(Prior art) In order to disperse the ink in an aqueous solvent after removing ink particles from fibers, thermal and mechanical energy were utilized in the presence of chemicals. Subsequently, the ink particles were separated from fibers by a rinsing process or a flotation separation process, or a modernistic process comprising the two processes.

The chemicals used in the conventional de-inking process are surfactants having an action of ink removal by rinsing, a dispersing action in which the deposition of ink on the fiber surface was prevented by retaining the ink particles, and a foaming action for foam flotation separation.

The typical surfactants are a long chain molecule having a hydrophobic part on one end and hydrophilic part on the other end, and they are the ones with a hydrophobic part comprised of fatty acids, aliphatic alcohols, alkyl phenol, and other oil-soluble surfactants.

Commonly, the hydrophilic part in de-inking surfactants is an anion molecule, such as carbonic acid salt or sulfonic acid salt, and a nonionic molecule, such as a polyoxyethylene chain.

The typical surfactants used in rinsing and foam flotation separation in a de-inking process are the sodium salt or potassium salt (soap) of a straight chain fatty acid, a linear alkyl benzene sulfonic acid salt (LAS), an olefin sulfonic acid salt, a long chain fatty acid alcohol, a polyoxyethylenated alkyl phenol, an alkyl phenol ethoxylate, and a polyoxyethylenated straight chain alcohol.

The main disadvantage of the use of a surfactant in the de-inking process is the excessive foaming in the subsequent pulp stock flow and in the papermaking process. Some of the surfactants mentioned above are resistant to the biological decomposition in the wastewater treatment and that is an important environmental problem.

In the foam flotation separation process, the ink particles are allowed to form large particles, which are then allowed to adhere on the surface of the air bubbles in the presence of a collecting agent.

The collecting agent is needed to provide an effective flotation separation, and commonly they are anionic long chain fatty acid soaps.

In the flotation chamber (cells), the lumped particles adhere on the foam from the aeration, and then they float up to the surface and are removed from that system.

end p.8-1 original translation

The main disadvantage in the flotation separation method using a fatty acid collecting agent is the deposition of pitch and calcium scale formation in the raw material lines and in the papermaking process apparatus. The other chemicals, other than the surfactants, are sodium hydroxide, sodium silicate, metal ion chelate, and hydrogen peroxide.

A hydrogen peroxide-base bleaching agent prevents the yellowing of pulp caused from the addition of sodium hydroxide and its addition is necessary in improving the brightness of the pulp fibers.

Due to the progresses in the printing technology and copying technology, the conventional de-inking process utilizing a surfactant faces a great problem in the processing of waste papers printed by a highly polymerized ink or non-impact printing ink, namely, waste paper printed on by ultraviolet application, thermal setting printing, Xerox printing, and ink jet printing.

Those inks commonly contain cured polymer resin, and the ink particles are bound on the fiber surface so tightly so that the complete ink removal in the waste paper defiberizing process may not be possible. Therefore, it requires an excess thermal energy and mechanical energy in addition to the presence of the inefficacious, conventional chemical reagents.

In the conventional flotation separation de-inking of waste newsprint, the main technical problem is related to the ink particles filled in the fiber bundles and between the fine fibers. The removal of those particles by rinsing and/or flotation separation process is almost impossible.

(Problems to be solved by invention)
This invention provides an effective new, improved de-inking method for the de-inking from waste newsprint and other printed paper containing no lignin, namely, white ledger paper, laser printed paper by electrostatic photographic process, and computer printout paper.

(Means for solving problem)
The invention de-inking process is an ink particle removal process utilizing the enzymic biochemical action on the surface of the cellulose fibers and the dispersion function of the enzyme protein on the ink particles.

In comparison with a conventional method, it does not require alkaline and de-inking surfactants, but in order to increase the de-inking efficiency, an enzyme can be used in conjunction with a surfactant. In the foam flotation separation, it requires no fatty acid collecting agent. In de-inking of newsprint, sodium hydroxide was not used, and therefore the use of hydrogen peroxide was not needed to prevent yellowing.

In the conventional flotation separation of newsprint de-inking process, the main technical problem was related to the ink particles in the fiber bundles and between the fine fibers. The removal of those particles by rinsing and/or flotation process from the fibers is almost impossible.

(Problems to be solved by invention)
This invention provides an effective new, improved de-inking method for the de-inking from waste newsprint and other printed paper containing no lignin, namely, white ledger paper, laser printed paper by electrostatic photographic process, and computer print out paper.

(Means for solving problems)
The invention de-inking process is an ink particle removal process utilizing the enzymic biochemical action on the surface of the cellulose fibers and the dispersion function of the enzyme protein on the ink particles.

In comparison with a conventional method, it does not require alkaline and de-inking surfactants, but in order to increase the de-inking efficiency, an enzyme can be used in conjunction with a surfactant. In the foam flotation separation, it requires no fatty acid collecting agent. In de-inking of newsprint, sodium hydroxide was not used, and therefore the use of hydrogen peroxide was not needed to prevent yellowing.

The addition of a fatty acid collecting agent in the biochemical de-inking process serves to solve the deposition of sticky pitch and the scale formed by the reagents involved in the conventional flotation separation process, such as the type of soap, calcium salt, and silicates used.

The invention method will be discussed in detail below.

Newsprint, such as waste newsprint or waste printed paper containing no lignin, containing common pulp content (4 – 7% concentration) or high pulp content (12 – 15% concentration), is disintegrated in water at temperatures ranging from room temperature to 60°C.

The amount of the addition of enzyme is based on the dry weight of waste paper and the enzyme concentration is 0.005 – 5.0%. The pH of the starting slurry is controlled at 3.0 – 8.0. In comparison with the pulping process using sodium hydroxide and a surfactant, in the invention method utilizing an enzyme in the pulping process, the pulping time can be completed within a comparatively short time, and the ink particles are completely separated from the surface of fibers and dispersed well.

The dispersed ink can be removed from pulp fibers using a conventional rinsing apparatus without the aid of a surfactant, namely, by using a vibrating sieve and a drum rinsing apparatus. By the action of enzyme protein, the dispersed ink particles in the diluted slurry can be selectively removed by using a conventional flotation separation apparatus by the action of bubbles, which float up the particles, resulted from the injection of air and the adsorption of the air into the slurry. In the case of waste newsprint, the use of a fatty acid collecting agent is not needed, but in the case of laser printed paper, a small amount of fatty acid collecting agent may be added to improve the de-inking efficiency.

(Action)

In the biochemical de-inking process, in comparison with the pulping in the absence of an enzyme, the pulping time is significantly shortened, therefore, the energy consumption for the pulping process can be reduced by almost 50%.

In the presence of an enzyme, it was observed that the pulping was faster and easier. The presence of an enzyme inhibits the cohesion of fibers, inhibits the adhesion of ink on the fiber surface and removes ink from the fiber bundles and between the microfibers. Apparently, these effects may be due to the characteristic biochemical activity of the enzyme

It is not known if a partial hydrolysis might take place in the cellulose in the microstructure of the fiber surface during the pulping stage. Due to the biochemical action of the enzyme, the fine ink particles filled in the fiber bundles and in the microfibers can be extracted, and such extraction was not possible by the uses of the conventional de-inking chemicals in de-inking of waste newsprint.

According to this biochemical de-inking of waste newsprint, the addition of hydrogen peroxide is not needed to prevent the yellowing of fibers. By this method, the cost of de-inking chemicals was significantly reduced when compared with that of a conventional process using sodium hydroxide, hydrogen peroxide, chelate and sodium silicate.

It must be pointed out that, in addition to the higher brightness of the resulting pulp, the pulp prepared by the invention method has higher physical strength than the pulp prepared by a conventional method. It is apparent that the addition of an enzyme did not deteriorate the strength of the fibers; rather, the strength has been improved by an unknown reason.

Examples

Example 1. De-inking of waste newsprint by cellulose decomposition enzyme

A portion of waste newsprint sample was added to pulp to give 4% concentration, and a portion of water at 40°C was added. Then cellulase was added to give 1% content, on the basis of the oven-dried weight of the waste paper, and allowed to soak for 10 minutes and then allowed to disintegrate for five minutes. After the completion of the disintegration process, one half of the pulp slurry was diluted to give 1% concentration.

The diluted pulp slurry was transferred to an air flotation separation chamber and air was injected in through a porous plate while collecting the ink-adhered floating foams as residue, and then the dispersed ink particles were separated from the slurry. The flotation period for a complete separation of ink bubbles was one minute. The remaining half of the slurry was rinsed off using a vibrating sieve to separate the ink particles.

The recycled pulp fibers obtained from the floatation separation process and from the rinsing process were evaluated for their brightness and mechanical strength. In order to compare the characteristics of the enzyme treated de-inked pulp against the conventionally de-inked pulp, the above waste paper was treated in a pulp slurry containing 1.0% NaOH, 0.3% H_2O_2, 3% sodium silicate solution (water glass), and 0.8% SERFAX MT-90 (fatty acid soap) and 0.2% IGEPAL-660, where the amount was based on the oven-dried weight basis of the waste paper. It took 10 minutes to achieve a complete disintegration for pulping. The resulting pulp was diluted to 1% concentration to disperse the ink particles by the method described above, i.e., flotation separation process using an experimental flotation chamber.

As shown in Table 1, the brightness of the de-inked pulp using the invention enzyme process was significantly higher than the brightness of the de-inked pulps using the conventional chemicals or by

using alkali-resistant cellulase. Also, the mechanical strength of the enzyme de-inked pulp was superior to the mechanical strength of the de-inked pulp obtained by using fatty acid collecting agent and dispersant (IGEPAL-660).

A microscopic observation clearly showed that the pulp prepared by the invention showed long chopped fibers, smoother fiber surface, and lesser mechanical damage.

[Table 1] Comparisons of properties of the pulps prepared by the invention method and conventional method

Trd p.8-9 orig = harder

KNOP: Domestic waste newsprint. ANOP: Waste newsprint in USA.
For the enzyme treated pulp, the flotation separation de-inking was cleaner and brighter than those by rinsing method.

It appears that the addition of an enzyme greatly accelerated the disintegration of waste paper. When waste newsprint was disintegrated at 4% concentration in a conventional pulp, the pulping time for the complete disintegration with the addition of 0.5% enzyme was 30 seconds as compared to five minutes (without the enzyme addition).

[Table 2] Relation of enzyme addition to disintegration time

Example 2. De-inking of laser CPO (computer printout) paper using cellulase.

The complete de-inking of waste laser CPO paper, which contains laser beam cured ink particles, using the conventional chemicals was almost impossible. The reason is that the ink particles were adhered so strongly on the surface of the fibers that the conventional chemicals, namely, alkali and common de-inking surfactant, were unable to separate the ink from the pulp slurry.

A portion of waste laser CPO paper sample was added to give 12.5 % in a high concentration pulp, and cellulase was added to the above to give 0.2% concentration, on the basis of the dried paper weight.

The pulping process was carried out for 20 minutes at starting material temperature of 20 - 35°C. The completely disintegrated pulp slurry was diluted to give 0.5% concentration, and subsequently, the dispersed ink slurry was separated according to the procedure described in Example 1 using the experimental flotation chamber.

In this case, a small amount of conventional fatty acid collecting agent and 0.3% of SERFAX MT-90, on the basis of dried waste paper weight, was added prior to the flotation separation to improve the de-inking efficiency and to increase the selectivity. Then it was subjected to a flotation separation for three minutes. To compare with the enzyme de-inked pulp, it was processed according to the conventional de-inking method. The treatment was carried out according to the chemical conditions listed below.

A 1% NaOH, 1% IGEPAL-660 dispersant, and 0.8% SEFAX MT-90, on the basis of the dried waste paper, were added.

Pulping temperature: 50°C,
Pulping time: 30 minutes,
Amount of calcium salt in flotation separation chamber: 200 ppm,
end Flotation separation time: 3 minutes,
Brightness and strength are listed in Table 3.

p. 8-9 orig'nl translat

As demonstrated in the table, the image analysis of the paper sample showed that the number of the residual ink particles were about 10-times less and the tensile strength was higher in the enzyme de-inked pulp than those of the pulp prepared by the uses of the conventional chemicals.

As far as the wastewater and the fiber strength are concerned, a high quality recycled chemical pulp can be obtained by the uses of a small amount of fatty acid collecting agent in conjunction with the uses of an enzyme.

[Table 3] Comparisons of characteristics of pulps prepared by invention method and conventional method.

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2. p. 8-10 original transl

Example 3. De-inking of waste newsprint using pectinolytic enzyme

As described in Example 1, waste newsprint containing 0.1% pectinase was immersed for 10 minutes at 40°C. The disintegrated pulp was diluted to give 1% concentration and the ink particles were subjected to flotation separation for one minute.

As shown in Table 4, the sheet of paper prepared according to the invention was bright and had improved tensile strength.

[Table 4] Comparisons of pectinolytic enzyme method and conventional method

(57) Scope of patent claims

Claim 1.

A waste paper recycling method using a biochemical de-inking method is characterized in that the method waste printed paper is maintained at pH 3 – 8 range and is pulped in the presence of an enzyme, and the ink particles are removed by flotation and /or rinsing method from fibers.

Claim 2.

The waste paper recycling method using a biochemical de-inking method described in Claim 1 is characterized in that the enzyme used in the method in Claim 1 is cellulase and/or pectinase.

Claim 3.

The waste paper recycling method using a biochemical de-inking method described in Claim 1 and Claim 2 is characterized in that the amount of an enzyme added is 0.005 – 5% range, on the basis of the dried weight of waste paper.

Claim 4.

The waste paper recycling method using a biochemical de-inking method in Claim 1 is characterized in that the temperature in the pulping process is maintained from room temperature to 60°C range.

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Title of invention	고지의생물학적탈묵에의한재생방법 (BIOLOGICAL DE-INKING METHOD)
Abstract	<목적>신문 용지 탈잉크 및 목재는 포함하지 않는 인쇄된 고지, 예를 들어 화이트레지, 레이저 인쇄된 정전 사진법의 카피 용지 및 컴퓨터의 프린트 아웃 고지에서 유효한 신규의 그리고 훨씬 개량된 탈잉크법을 제공한다. <구성>신문, 예컨데 헌 신문 용지 또는 인쇄된 목재를 포함하지 않는 고지를 통상의 펄프(농도 4-7%)중에서 또는 고농도 펄프(12-15%)중에서 실온에서 섭씨 60도까지의 범우의 수온으로 분해한다. 효소의 첨가 수준은 고지의 건조 중량을 기준으로하여 0.005-5.0%이며, 원료 슬러리의 pH는 3.0-8.0의 범위로 조절한다. 분산된 잉크는 일단 및 다단으로 세정력 있는 계면활성제의 도움없이 통상의 세정 프로세스 장치를 사용해서 펄프 섬유에서 제거되며 통상의 부선 장치에 의해 희석된 펄프 슬러리에서 선택적으로 제거할 수 있다. 헌 신문 용지의 경우에는 지방산 포집제가 필요 없으나 레이지 인쇄된 고지의 경우에는 잉크 제거 효율을 높이기 위해서 소량의 지방산 포집제를 첨가해도 좋다. <효과>효소의 첨가로 펄프화 시간을 상당히 감소시켜 거의 50% 정도의 감소폭으로 펄프화 에너지를 저하시킬 수 있다.
Representative Claim	고지와 효소를 첨가하여 펄핑하고 부상부유법이나 세척법에 의해 잉크입자를 제거후 초지하여서된 고지의 생물학적 탈묵에 의한 재생방법.

Representative Drawing	-
Full-Doc. of Unexamined Publication	View Full-Doc. of Unexamined Publication
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(54) 고지의 생물학적 탈묵에 의한 재생방법

요약

요약없음

명세서

[발명의 명칭]고지의 생물학적 탈묵에 의한 재생방법 [발명의 상세한 설명](산업상의 이용분야)본 발명은 탈잉크 프로세스에서 생화학적 방법에 의해 목재를 포함 또는 목재를 포함하지 않은 고지에서 유용한 펄프 섬유를 재생하는 방법에 관한 것이다.

펄프 섬유의 탈잉크는 본질적으로 잉크를 오물로 간주하고, 오물을 제거 또는 깨끗이 하는 프로세스이다.

(종래의 기술)섬유에서 잉크 입자를 제거하고 그리고 이들을 수성 용매중에 분산시키기 위해서는 열 및 기계적 에너지와 함께 화학약품을 사용한다. 다음에 세정 또는 부선에 의해 혹은 이들의 두개의 요소를 조합한 현대적 혼성 프로세스를 사용함에 의해 잉크 입자를 펄프 섬유에서 분리한다.

종래의 탈잉크 프로세스를 위해 사용되는 약품은 그의 기능이, 섬유에서 잉크를 제거하는 세정성, 분산하여 잉크 입자를 보지하여 섬유위에 재퇴적하는 것을 방지하는 분산작용, 그리고 잉크 입자의 포부선(泡浮選)에서 반포 작용이 있는 계면활성제이다.

전형적인 계면활성제로는, 일단에 소수성 부분을 그리고 타단에 친수성 부분을 갖는 장쇄 분자이다. 소수성 부분은 지방산, 지방족 알코올, 알킬페놀 또는 기타의 유용성 계면활성제로 이루어져 있다.

탈잉크 계면활성제중의 친수성 부분은, 통상은 음이온 분자 예컨대 카르본산염 또는 술폰산염 그리고 비 이온 분자 예컨대 폴리옥시에틸렌 연쇄로 구성된다.

세정 및 포부선 탈잉크 프로세스에서 보통 사용하는 전형적인 계면활성제는, 직쇄 지방산의 나트륨 및 칼륨염(비누), 선상 알킬벤젠술폰산염(LAS), 올레핀술폰산염, 장쇄 지방족 알코올, 폴리옥시에틸렌화 알킬페놀, 알킬페놀에톡실레이트, 그리고 폴리옥시에틸렌화 직쇄 알코올이다.

탈잉크 프로세스에서 이들의 계면활성제를 사용하는 주요한 불이익은, 후속하는 펄프 원료(STOCK) 플로 및 제지 프로세스 라인에서 과도한 발포(發泡)이다. 상기 계면활성제의 어떤 것은, 배수 처리단계에서 생물분해에 저항성이 있어 중대한 환경문제를 일으킨다.

포부선 탈잉크 프로세스에서는, 잉크를 큰 입자의 덩어리로 하고 이들을 공기의 거품에 부착시키기 위해 포집제를 첨가한다.

포집제는 효과적인 부선키 위한 필요하고 그리고 통상은 음이온성 장쇄 지방산 비누이다. 지방산 포집제는 칼슘 이온과 함께 침전하여 보다 큰 불용성 잉크 입자 및 포집제 입자를 형성한다.

부선실(cells)에서 공기의 주입에 의해, 덩어리가 된 입자가 거품에 부착하고, 표면에 뜨고 그리고 시스템에서 뜨게 하여 제거된다.

지방산 포집제를 사용하는 부선법의 주요한 결점은, 후속하는 원료 라인 및 제지 프로세스 장치에서 피치퇴적 및 칼슘의 스케일 부착 문제가 있다 계면활성제 이외의 기타 약품은, 가성소다, 나트륨실리케이트, 금속이온 킬레이트제 및 과산화수소이다.

과산화수소 표백제는, 가성소다의 첨가에 의해 일으키는 펄프 색의 황변을 막고 펄프 섬유의 밝이(brightness)를 개선하기 위해 첨가하지 않으면 안된다.

현대의 인쇄 기술 및 복사 기술에 있어서의 진보에 의해 계면활성제의 도움에 의한 종래의 탈잉크는, 다량으로 퍼곡된 고도로 중합한 또는 비충격(nonimpact) 잉크, 예컨대 자외선, 히트세트, 제록스, 레이저 및 잉크 제트의 사용에 의해 인쇄된 고지(故紙)에 관해서 중대한 문제에 부닥친다.

이들의 잉크는 통상 경화한 폴리머 수지를 포함하고, 이것은 종래의 탈잉크 화학품에 의해 고지의 섬유해체(defiberizing)(펄프화) 단계의 사이에 완전히 잉크를 제거하는 것을 불가능으로 할만큼 세게 잉크 입자를 섬유 표면상에 결합한다. 효과가 없는 종래의 화학품에 더하여 과잉의 열 및 기계적 에너지도 또 필요하게 된다.

신문용지의 고지를 위한 종래의 부선(浮選) 탈잉크 프로세스에서는, 부된 기술적 문제는 섬유의 다발중에 그리고 소섬유의 사이에 메워진 가는 잉크 입자와 관계하고, 이들의 입자는 세정 및/또는 부선 프로세스에 의해 섬유에서 제거하는 것은 거의 불가능하다.

(발명의 해결하려고 하는 과제)본 발명은 신문용지 탈잉크 및 목재는 포함하지 않는 인쇄된 고지, 예컨대 화이트레지(Whiteledger), 레이저 인쇄된 정전 사진법의 카피 용지 및 컴퓨터의 프린트 아우트 고지에서 유효한 신규의 그리고 훨씬 개량된 탈잉크법을 제공한다.

(문제를 해결하기 위한 수단)본 발명의 탈잉크법은 셀룰로오스 섬유 표면에 대한 효소의 생물학적 작용 그리고 잉크 입자에 대한 효소 단백질의 분산기능의 사용에 의해 잉크 입자를 제거하는 것이다.

종래의 방법과는 대조적으로, 알칼리 및 탈잉크 계면활성제를 필요로 하지 않으나, 탈잉크 효율을 늘리기 위하여 효소와 같이 있는 어떤 종류의 계면활성제를 사용할 수도 있다. 포부선 프로세스에서는, 지방산 포집제를 필요치 않는다. 신문용지 탈잉크에서는 가성소다를 사용하지 않으므로 황변 방지를 위한 과산화수소 표백제도 또 필요치 않는다.

이 생물학적 탈잉크 프로세스에서의 지방산 포집제의 배제는, 지방산 타입의 비누 및 칼슘염 및 실리케이트를 사용하는 종래의 부선 프로세스에 부수하는 끈질긴 피치 및 스케일 퇴적문제를 해결할 것이다.

본 발명의 방법을 아래에 상세히 진술한다.

신문, 예컨대 헌 신문용지 또는 인쇄된 목재를 포함하지 않는 고지를 통상의 펄퍼(농도 4~7%)중에서 또는 고농도 펄퍼(12~15%)중에서 실온에서 60℃까지의 범위의 수온으로 분해한다.

효소의 첨가 수준은 고지의 건조 중량을 기준으로 하여 0.005~5.0%이며, 원료 슬러리의 pH는 3.0~8.0의 범위로 조절한다. 가성소다 및 계면활성제를 사용하는 종래의 펄프화 프로세스와 비교하여 효소의 본 방법에서의 펄프화는 비교적 짧은 시간으로 완결할 수가 있고, 그리고 잉크 입자는 섬유 표면에서 완전히 분리되고 그리고 잘 분산된다.

분산된 잉크는 일단 및 다단으로 세정력있는 계면활성제의 도움없이 통상의 세정 프로세스장치, 예컨대 진동체 및 드럼 세정기에 의해 펄프 섬유에서 제거된다. 효소 단백질의 작용에 의해 분산된 잉크 입자도 또, 공기가 펄프중에 주입 또는 흡입되어 거품이 생겨 입자를 잡아올리는 통상의 부선장치에 의해, 희석된 펄프 슬러리에서 선택적으로 제거할 수가 있다. 헌 신문용지의 경우에는 지방산 포집제를 필요치 않는다. 그러나 레이저 인쇄된 고지의 경우에는 잉크 제거 효율을 늘리기 위해 소량의 지방산 포집제를 첨가해도 좋다.

(작용)이 생물학적 탈잉크 프로세스는 효소의 비존재하에서의 펄프화에 비하여 효소의 첨가 결과로서 펄프화 시간을 상당히 감소시켰으므로 대폭으로, 예컨대 거의 50%나 감소폭으로 펄프화 에너지를 저하시킬 것이다.

효소의 존재하에서의 관찰된 더 빠르게 그리고 더 용이한 펄프화는, 섬유의 결합을 해합하고 그리고 섬유표면상에 결합하고 또한 섬유의 다발 내부의 또는 소섬유의 사이의 잉크를 떼는데 효과적인 효소의 특이한 생물학적 활성에 기인하는지도 모르겠다.

섬유 표면의 미소 구조내의 셀룰로오스와 부분적인 효소에 의한 가수분해가 펄프와 단계의 사이에 일어나는지 모르겠다. 효소의 이 생물학적 활성때문에, 헌 신문용지 탈잉크때는 종래의 탈잉크 화학품에 의해서는 끄집어내기가 불가능했던, 섬유의 다발, 소섬유 및 미섬유 내부에 메워진 미세한 잉크 입자를 끄집어 낼 수가 있다.

헌 신문용지의 이 생물학적 탈잉크법에 의하면, 섬유의 황변을 막기 위한 과산화수소의 첨가가 필요없고, 이것은 가성소다, 과산화수소, 킬레이트제 및 나트륨 실리케이트를 사용하는 종래의 탈잉크 프로세스와 비교하여 탈잉크 화학품 코스트가 상당한 삭감을 결과로서 가져올 것이다.

생성하는 펄프의 훨씬 높은 밝이에 더하여 본 발명의 방법에 의해 제조되는 생성하는 펄프 섬유의 물리적 강도의 성질이 종래의 방법에 의해 제조되는 대응하는 펄프의 성질보다도 높은 것이 발견되는 것을 지적해야 할 것이다. 효소의 첨가는 섬유의 강도를 열화하지 않는 것같이 보이고, 오히려 아직 미지의 이유에 의해 섬유의 강도를 개선한다.

실시예 실시예 1셀룰로오스 분해 효소에 의한 헌 신문용지의 탈잉크 헌 신문용지 고지의 샘플을 펄프에 첨가하고, 그것을 4% 농도에서 40℃의 물로 채우고, 그리고 고지의 오븐 건조 중량을 기준으로 하여 0.1%의 투약 수준으로 셀루라아제를 용해했다. 이 고지를 10분간 침지하고, 그리고 다음에 5분간 해체했다(disintegrated). 고지의 완전한 해체후에 펄프 슬러리의 반을 1% 농도로 희석했다.

희석한 펄프 슬러리를 공기 부선실로 옮기고, 그리고 다음에 다공성의 판을 통하여 공기를 주입하면서 잉크 입자 거품은 부선실에서 뜬 찌꺼기로 하여 집어낸다는 것으로써 분산한 잉크 입자를 펄프 슬러리에서 제거했다. 잉크의 거품의 완전한 제거를 위한 부선시간은 1분이었다. 펄프 슬러리의 나머지 반을 실험용 진동체로 세정하여 분산한 잉크 입자를 제거했다.

부선 및 세정 공정에 의해 얻어진 생성하는 재생된 펄프 섬유를 펄프의 밝이 및 기계적 강도 특성에 관하여 평가했다. 이 효소 처리된 탈잉크 펄프를 종래의 탈잉크 펄프와 비교하기 위해 고지의 같은 샘플을 고지의 오븐 건조 중량을 기준으로 하여 1.0% NaOH, 0.3% H

$_2O_2$, 3% 나트륨 실리케이트용액(물유리) 및 0.8%의 세르팍스(SERFAX) MT-90(지방산 비누)와 0.2% 아이게팔(IGEPAL)-660을 첨가한 펄프중에서 처리했다. 완전한 해체를 위한 펄프화 시간은 10분간이었다. 1% 농도로 희석한 후, 분산한 잉크 입자를 위에 말한 방법과 같이 하여 실험용 부선실에 의한 부선법에 의해 제거했다.

표 1중에 나타내는 것 같이, 본 발명의 효소에 의해 탈잉크한 펄프의 밝이는 종래의 화학품이나 알칼리 내성 셀루라아제에 의해 탈잉크한 펄프의 밝이 보다 훨씬 높고, 그리고 효소 탈잉크 펄프의 기계적 강도도 또 지방산 포집제 및 분산제(아이게팔-660)에 의해 탈잉크한 펄프의 기계적 강도 보다도 우수했다.

현미경으로서의 관찰에 의해 본 발명에 의해 제조된 펄프는 보다 긴 섬유 단편을 포함하고, 그리고 보다 매끄러운 섬유 표면을 갖고 그리고 기계적인 손상이 보다 적은 것이 명백해졌다.

[표1]본 발명의 방법 및 종래의 방법에 의해 재생된 펄프의 성질 비교

KNOP : 한국의 헌 신문용지 ANOP : 미국의 헌 신문용지효소 처리한 펄프는 부선 잉크 제거와 비교하여 세정에 관해서 보다 깨끗한 그리고 밝은 펄프를 주었다.

효소의 첨가는 고지의 해체를 대폭으로 가속하는 것 같이 보였다. 헌 신문용지를 4% 농도에서 통상의 펄퍼중에서 해체한 때, 표 2에 나타내는 것 같이 0.5%의 효소의 첨가는 완전한 해체를 위한 펄프화 시간을 5분(효소 첨가없음)에서 30초로 감했다.

[표 2]효소 첨가와 해체 시간과의 관계

실시예 2셀룰로오스 분해 효소에 의해 레이저 CPO(컴퓨터 프린트 아우트)의 탈잉크 종래의 탈잉크 화학품에 의해 레이저 CPO 고지에서 레이저빔 경화한 잉크 입자를 완전 제거하는 것을 달성하는 것은 거의 불가능하다. 왜냐하면, 종래의 탈잉크 화학품에서 알칼리 및 일반의 탈잉크 계면활성제가 펄프수 슬러리중으로 떼내고, 그리고 분산할 수가 없을 정도 강하게 잉크 입자가 섬유 표면에 점착해 있기 때문이다.

레이저 CPO 고지의 샘플을 실험용 고농도 펄프풍의 물에 12.5%의 농도로 첨가하고, 그리고 셀루라아제를 종이의 건조 중량을 기준으로 하여 0.2%의 투약 수준으로 이물에 첨가했다.

20~35℃ 이상의 원료 수온으로, 펄프화를 20분간 실시했다. 완전히 해체된 펄프 슬러리를 0.5%로 희석하고 그리고 다음에 분산된 잉크 입자를 실시예 1에서 설명한 것과 같이 하여 실험용 부선실을 사용하여 펄프 슬러리에서 제거했다.

이 경우에 있어서는, 잉크 제거 효율 및 선택성을 늘리기 위해 소량의 통상의 지방산 포집체, 고지의 건조중량을 기준으로 하여 0.3%의 세르팍스 MT-90을 공기 부선에 앞서 첨가하고, 그리고 부선 시간은 3분이었다. 효소 탈잉크 펄프와 비교하기 위해 종래의 탈잉크 펄프와 같은 방법으로써, 단 아래와 같은 다른 화학적 조건에서 제조했다.

고지의 건조 중량을 기준으로 하여 1% NaOH0.1% 아이게팔 660 분산제

0.8% 세르팍스 MT-90

펄프화 온도 : 50℃펄프화 시간 : 30분 부선실에의 칼슘염의 첨가 : 200ppm부선시간 : 3분 생성하는 펄프 샘플의 밝기 및 강도의 성질을 표 3에서 비교했다.

이 표에 나타나듯이, 종이 샘플의 상(image) 분석은, 잔류 잉크 입자의 수는 효소에 의해 탈잉크한 펄프에 관해서 훨씬, 약 10배나 적고 그리고 인장 강도도 또 종래의 화학품에 의해 제조된 펄프와 비교하여 보다 높았던 것을 나타낸다.

오물수 및 섬유의 강도의 성질에 관해서 고품질의 재생된 화학적 펄프는 부선법에 의해 소량의 지방산 포집제와 조합한 효소의 사용에 의해 얻을 수가 있다.

[표 3]본 발명의 방법 및 종래의 방법에 의해 재생된 펄프의 성질의 비교

실시예 3펙틴분해(Pectinolytic) 효소에 의한 헌 신문용지의 탈잉크 실시예 1과 같은 방법으로 0.1%의 펙티나아제를 포함하는 헌 신문용지를 40℃에서 10분간 침지하고 그리고 5분간 해체했다. 해체된 펄프를 1%로 희석하고, 잉크 입자를 부선에 의해 1분간 제거한다.

표 4에 나타냈듯이 본 발명의 방법에 의해 제조된 종이 시트의 밝이 및 인장강도는 개량돼 있다.

[표 4]펙틴분해 효소를 사용하는 방법과 종래의 방법과의 비교

(57) 청구의 범위

청구항1

고인쇄지를 pH 3~8의 범위에 제어하고 효소에 의해 펄프화하고, 그리고 부선 및/또는 세정법에 의해 섬유에서 잉크 입자를 제거하는 것을 특징으로 하는 고지의 생화학적 탈묵에 의한 재생방법.

청구항2

제 1항에 있어서, 효소로서 셀루라제 및/또는 펙티나제를 사용하는 것을 특징으로 하는 고지의 생화학적 탈묵에 의한 재생방법.

청구항3

제 1항 또는 제 2항에 있어서, 고인쇄지의 건조 중량을 기준으로 하여 0.005~5%의 범위의 양의 효소를 첨가하는 것을 특징으로 하는 고지의 생화학적 탈묵에 의한 재생방법.

청구항4

제 1항에 있어서, 펄프화 프로세스의 온도를 실온에서 60℃까지의 범위로 제어하는 것을 특징으로 하는 고지의 생화학적 탈묵에 의한 재생방법.

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